A NMR STUDY OF *N,N,N',N'*-TETRAETHYLTHIURAM DISULFIDE AND ITS COMPLEXES WITH ZnI_2, CdI_2 and HgI_2

BY

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The thermodynamic constants of the hindered rotation around the $S_2C—NR_2$ bond of *N,N,N',N'*-tetraethylthiuram disulfide and its complexes with Zn, Cd and Hg(II) halides have been obtained by NMR.

It is shown that the effect of the solvent on the rotation rate is small.

At low temperatures the NMR patterns reveal the existence of a second process that interchanges inequivalent ethyl groups. This process is due to the non-equivalence of the ligand sulfur atoms as can be seen from the crystallographic structure of HgI_2 (Me_4tds). The thermodynamic constants of the interconversion between these two inequivalent configurations are also presented.

1. Introduction

In a previous paper by *Brinkhoff* et al.[1] the magnetic inequivalence of the alkyl groups a and b of *N,N,N',N'*-tetra-alkylthiuram disulfide, R_4tds (see Fig. 1) and its complexes with Zn, Cd and Hg (II) halides has been demonstrated.

At high temperatures the four alkyl groups of R_4tds were found to result in one single NMR pattern, while lowering the temperature resulted in a doubling of all NMR signals, due to slow rotation around the partially double $S_2C—NR_2$ bond.

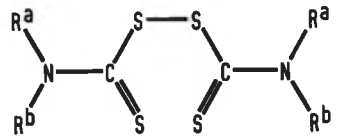

Fig. 1. R_4tds – structural formula.

[1] *H. C. Brinkhoff, A. M. Grotens* and *J. J. Steggerda*, Rec. Trav. Chim., **89**, 11 (1970).

The magnetic inequivalence of the groups a and b is enhanced upon complexation of the ligand with various metal halides[1] and depends on the solvent.

We will show that the computer simulated spectra of Et_4tds, ZnI_2 (Et_4tds), CdI_2 (Et_4tds) and HgI_2 (Et_4tds) dissolved in various solvents using the model for a two sites problem agree extremely well with the experimental spectra measured in $CDCl_3$ and in C_6H_5Br. The simulated spectra enable determination of the thermodynamic constants for the hindered rotation around the $S_2C—NEt_2$ bonds.

At lower temperatures this rotation is frozen out at the NMR time scale; continued decrease of temperature reveals another intramolecular conversion process and now all four ethyl groups become non-equivalent. A model is proposed for this process and its thermodynamic constants are found from computer simulated spectra.

Table I

Proton NMR data of the spectra of Et_4tds and its complexes with ZnI_2, CdI_2 and HgI_2 in $CDCl_3$ and C_6H_5Br.

Compound dissolved in $CDCl_3$	δ_{CH_2} (ppm)		δ_{CH_3} (ppm)		
	1	2	1	2	T (°C)
Et_4tds	4.06	3.99	1.50	1.31	−20
ZnI_2 (Et_4tds)	4.64	4.40	2.04	1.80	+16
CdI_2 (Et_4tds)	4.70	4.44	2.04	1.80	+16
HgI_2 (Et_4tds)	4.67	4.45	2.08	1.76	+ 7.5
Compound dissolved in C_6H_5Br					
Et_4tds	4.13	3.99	1.47	1.33	−15
ZnI_2 (Et_4tds)	—	—	2.05	1.79	+ 8.5
CdI_2 (Et_4tds)	4.76	4.32	2.05	1.79	+ 8.5
HgI_2 (Et_4tds)	4.67	4.25	2.09	1.76	−15

$\delta = \frac{H_{comp} - H_{ref}}{H_{ref}} \times 10^6$; HMDS was the external standard.

Shift accuracy is about 0.01 ppm.

For multiplets the δ values for the centres have been tabulated; the intensity ratio of the signals 1 and 2 is always 1 : 1.

$J_{H-H_\alpha} = 7 \pm 0.5$ Hz; $1/T_{2,0} = 5.5 \pm 0.5$ rad/s.

2. Results and discussion

2.1. *The spectra at temperatures higher than +10°*

When the NMR spectra of solutions of Et_4tds, ZnI_2 (Et_4tds), CdI_2 (Et_4tds) and HgI_2 (Et_4tds) in $CDCl_3$ and in C_6H_5Br are measured at sufficiently low temperatures, the quartet for the CH_2 groups splits up into two quartets of equal intensity, CH_2^a and CH_2^b and the CH_3 triplet into two triplets CH_3^a and CH_3^b. The shifts of these groups, together with the temperatures required for maximum splitting are listed in Table I. It is not possible to attribute the measured chemical shift values to the positions a or b.

It should be noted that for the CH_2 groups the chemical shift difference $\Delta_{ab} = \delta_1 - \delta_2$ for the $CDCl_3$ solution of a certain compound is always about 50% of that observed for the corresponding C_6H_5Br solution.

As an example Fig. 2 demonstrates the drastic changes which occur in the NMR spectrum of CdI_2 (Et_4tds) in C_6H_5Br upon changing the temperature, due to the internal rotation process. In $CDCl_3$ the limit of fast exchange could not be reached, because of the low boiling point of $CDCl_3$ (+61°), however, in C_6H_5Br (b.p. + 156°) a fast exchange spectrum is obtained at 109° consisting of one quartet for the CH_2 and one triplet for the CH_3 groups.

All NMR spectra have been simulated by using the modified Bloch equations describing the exchange between two equally populated sites[2]. The simulation requires three independent parameters only, viz. $T_{2,0}^{-1}$, the line-width parameter in the absence of exchange, the lifetime τ of a particular configuration and the positions of the multiplets at conditions of very slow rotation ($\tau \to \infty$) (see Table I). $T_{2,0}^{-1}$ was chosen in such a way that the line shape of the CH_2 quartets is matched by that in the experimental spectra, *e.g.*, all spectra measured at temperatures higher than +10° could be simulated well with $T_{2,0}^{-1}$ equal to 5.5 rad/s. The lifetime τ at a given temperature was found by trial and error; it was varied until shape and position of the triplet(s) as well as the quartet(s) in the simulated NMR spectrum matched perfectly with those in the experimental spectrum. The computer simulations of the NMR spectra of CdI_2 (Et_4tds) in C_6H_5Br at temperatures higher than +10°, obtained following the described procedure, are presented in Fig. 2 in addition to the experimental spectra.

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[2] *J. A. Pople, W. G. Schneider* and *H. J. Bernstein*, High Resolution Nuclear Magnetic Resonance; McGraw-Hill, New York, 1959, Chapter 10.

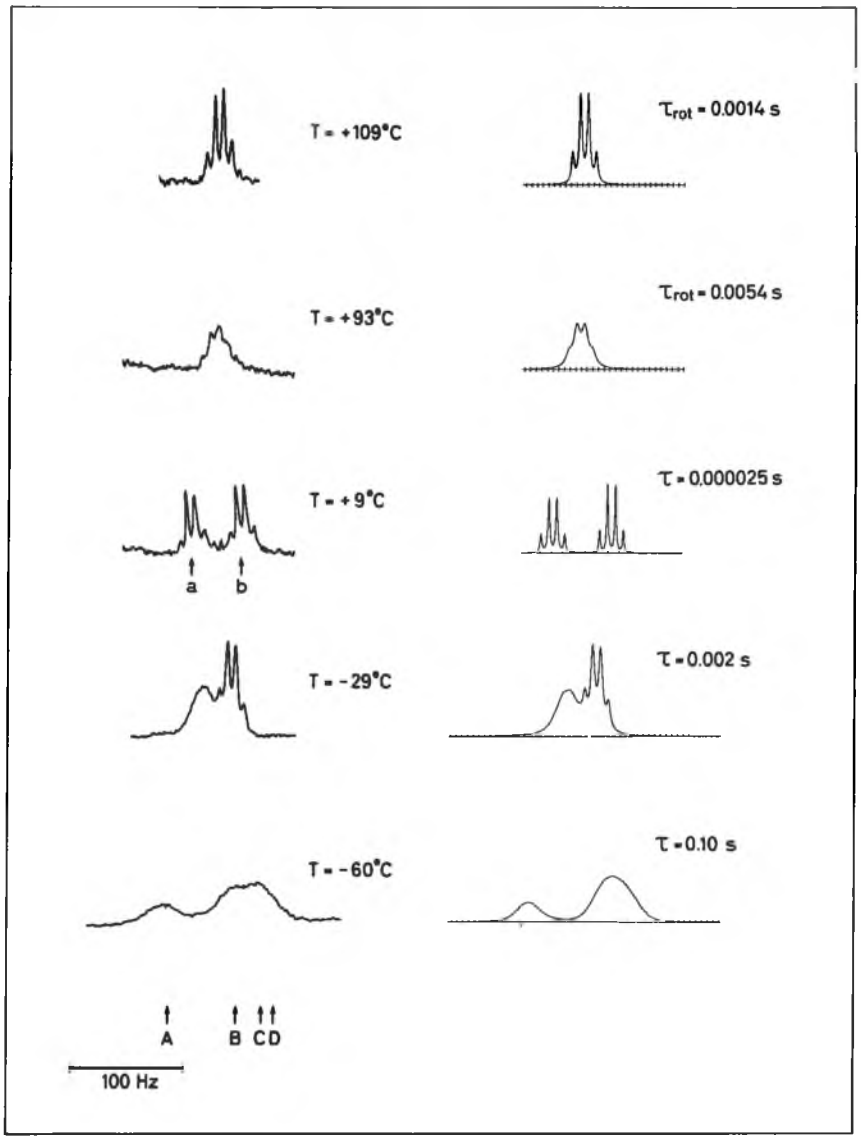

Fig. 2. Proton NMR pattern of the CH_2 groups in CdI_2 (Et_4tds) dissolved in $CDCl_3$ ($T < +10°C$ and in C_6H_5Br ($T > +10°C$) at various temperatures (left hand side) and computer simulations (right hand side). The spectra at $-29°C$ and $-60°C$ have been simulated with $T_{2,0}^{-1}$ equal to 14.0 and 14.6 rad/s, respectively.

2.2 *The spectra at temperatures lower than +10°*

When the temperature is sufficiently low an NMR pattern consisting of two quartets (CH_2^a and CH_2^b) and of two triplets (CH_3^a and CH_3^b) is obtained. For the case of CdI_2 (Et_4tds) and of HgI_2 (Et_4tds) a further decrease in temperature revealed a second exchange process that influences shape and position of the CH_2 signals only. The poor solubility of ZnI_2 (Et_4tds) at low temperatures in both $CDCl_3$ and C_6H_5Br resulted in spectra with poor signal to noise ratio, preventing further kinetic analysis.

Some low temperature spectra of CdI_2 (Et_4tds) in $CDCl_3$ are presented in Fig. 2. Upon lowering the temperature the low field CH_2 quartet broadens more than the high field one and yields a single structureless signal at $-45°$ whereas the high field multiplet can still be identified as a broadened quartet. At $-60°$ the spectrum shows three broad signals for all CH_2 groups.

The crystallographic structure of HgI_2 (Me_4tds) shows that the sulfur atoms in the seven-membered ring are not equivalent[3]. From a structure model one learns that a ring inversion process may interchange the positions of the sulfur atoms; consequently the two alkyl groups a and also the alkyl groups b interchange. The changes at low temperatures in that part of the spectra where the CH_2 groups resonate can be explained, as we will show, by this inversion process, using the same model as used for the rotation. That the ring inversion does not affect the CH_3 signals is probably due to the larger distance between the CH_3 group and the ring compared with that of the CH_2 group and the ring.

The three broad signals, representing the NMR pattern of all CH_2 groups in CdI_2 (Et_4tds) and HgI_2 (Et_4tds) at $-60°$, can be analyzed as a superposition of four signals A, B, C and D, the CH_2 groups with chemical shift δ_1 yielding A and D and the CH_2 groups with chemical shift δ_2 yielding B and C. The positions of the peaks A, B, C and D are given in Table II. The simulations have been carried out by adding the

Table II

Proton NMR data of the spectra of CdI_2 (Et_4tds) and HgI_2 (Et_4tds) in $CDCl_3$.

	δ_{CH_2} (ppm)				δ_{CH_3} (ppm)		T (°C)
Compound	A	B	C	D	A, D	B, C	
CdI_2 (Et_4tds)	5.16	4.60	4.28	4.23	2.04	1.80	−70
HgI_2 (Et_4tds)	5.06	4.59	4.31	4.28	2.08	1.76	−70

[3] *P. T. Beurskens, J. A. Cras, J. H. Noordik* and *A. M. Spruyt*, J. Cryst. Mol. Struct. **1**, 93 (1971).

line pattern, resulting from the interconversion between the two sites A and D, to that of the interconversion between the sites B and C, each process taken with a statistical weight of 1.0. In Fig. 2 the CH_2 absorption signals are shown for CdI_2 (Et_4tds) in $CDCl_3$ at temperatures lower than $+10°$ together with the simulations.

Spectra of CdI_2 (Et_4tds) and of HgI_2 (Et_4tds) in C_6H_5Br could be measured at temperatures as low as $-24°$ and they also demonstrated the existence of the second exchange process. Because of the high melting point of C_6H_5Br ($-31°$) this solvent did not permit measurement of spectra at conditions of very slow exchange ($\tau \rightarrow \infty$), consequently the values for $\Delta(\Delta_{AD} = \delta_A - \delta_D$ and $\Delta_{BC} = \delta_B - \delta_C)$ could not be obtained.

2.3. *Thermodynamic constants for the hindered rotation around the S_2C—NR_2 bonds*

Fig. 3 shows the Arrhenius plots for hindered rotation in Et_4tds, ZnI_2 (Et_4tds), CdI_2 (Et_4tds) and HgI_2 (Et_4tds) in $CDCl_3$. Similar plots are obtained for solutions of these complexes in bromobenzene. The thermodynamic constants derived from these plots are listed in Table III. The activation energy ΔE_{act} and $\log k_o$ are determined directly from the plots while the thermodynamic constants for the activated complex $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ result from application of the Eyring equation with a path degeneracy factor of 1.

Table III

Thermodynamic constants of the rotation around the S_2C—NR_2 bond in Et_4tds and its complexes with ZnI_2, CdI_2 and HgI_2 in $CDCl_3$ and in C_6H_5Br*.

Compound dissolved in $CDCl_3$	ΔE_{act} (kcal. mole^{-1})	$^{10}\log k_o$ (k_o in S^{-1})	$\Delta G^{\neq}_{273}$ (kcal. mole^{-1})	$\Delta H^{\neq}_{273}$ (kcal. mole^{-1})	$\Delta S^{\neq}_{273}$ (e.u.)
Et_4tds	20	16	18.5	20.0	+ 6
ZnI_2 (Et_4tds)	20	14	19.5	19.5	+ 1
CdI_2 (Et_4tds)	20	14	19.5	19.5	+ 1
HgI_2 (Et_4tds)	20	15	18.0	19.5	+ 5
Compound dissolved in C_6H_5Br					
Et_4tds	18	14	16.0	18.0	+ 7
ZnI_2 (Et_4tds)	17	13	17.0	17.0	− 1
CdI_2 (Et_4tds)	23	16	18.5	22.0	+12
HgI_2 (Et_4tds)	23	16	19.5	22.5	+14

* The inaccuracy in ΔE_{act}, $^{10}\log k_o$ and $\Delta S^{\neq}$ is approximately 1 unit; for $\Delta G^{\neq}$ and $\Delta H^{\neq}$ approximately 0.5 unit.

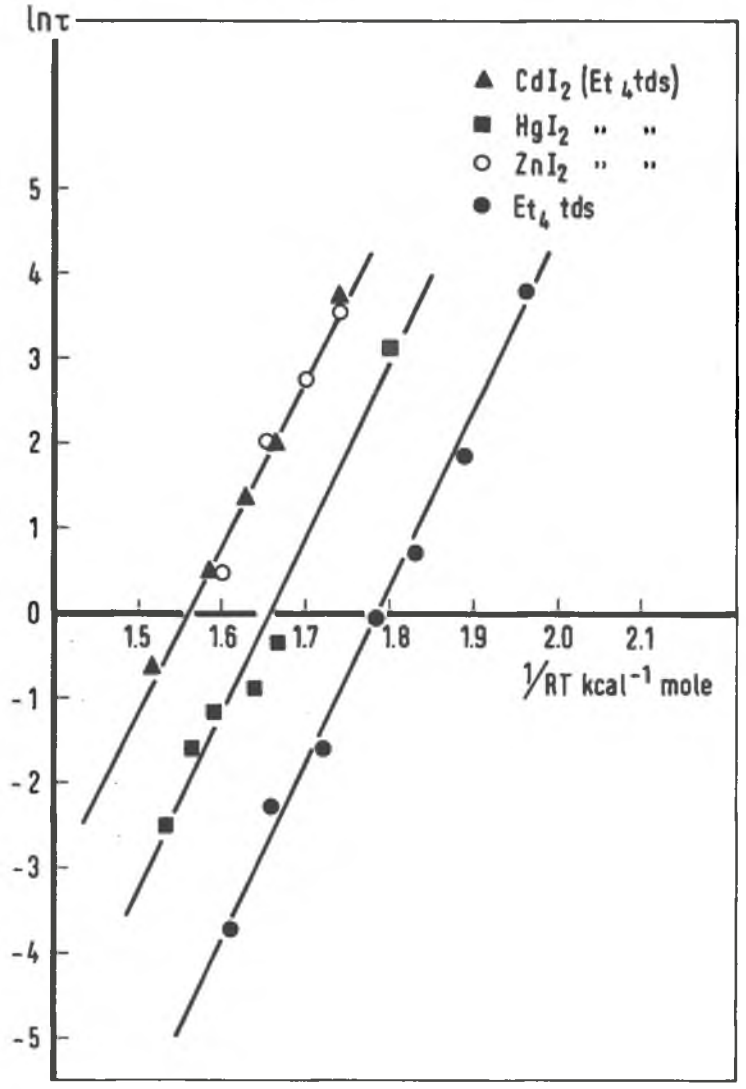

Fig. 3. Arrhenius diagram for the rotation around the $S_2C—NR_2$ bond in Et_4tds and its complexes with ZnI_2, CdI_2 and HgI_2, dissolved in $CDCl_3$.

The values for ΔE_{act} have the same order of magnitude as those found for other hindered rotation processes[4].

[4] *J. O. Sutherland,* Annual Reports on NMR spectroscopy, Vol. 4: Academic Press, London, 1971, p. 203.

2.4. *Thermodynamic constants for the ring inversion in CdI_2 (Et_4tds) and HgI_2 (Et_4tds)*

Fig. 4 shows the Arrhenius plots for the ring inversion in CdI_2 (Et_4tds) and in HgI_2 (Et_4tds) dissolved in $CDCl_3$. The thermodynamic constants derived from these plots are given in Table IV. The values for ΔE_{act} and $\Delta G^{\neq}$ have the same order of magnitude as those reported in the literature for inversions of rings containing hetero atoms[5].

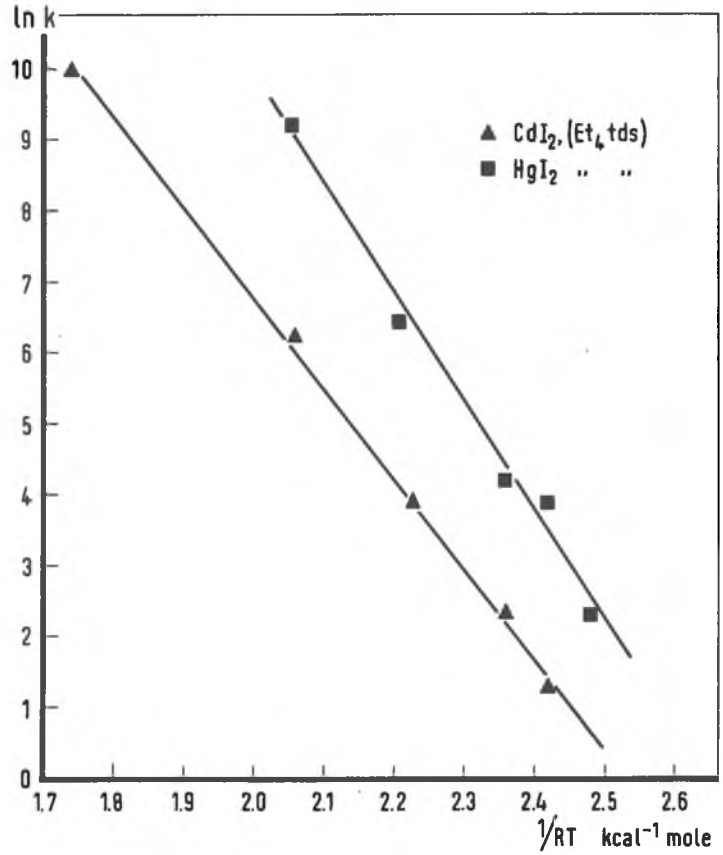

Fig. 4. Arrhenius diagram for the ring inversion in CdI_2 (Et_4tds) and HgI_2 (Et_4tds), dissolved in $CDCl_3$.

3. Experimental part

The ^1H NMR spectra were recorded on a Varian HA-100 spectrometer operating at 100 MHz. The computer simulations were calculated on an IBM 360/50 computer.

For Et_4tds and its complexes with ZnI_2, CdI_2 and HgI_2, which were prepared as described in the literature[1,6], the agreement with the published melting points was taken as evidence of purity.

Table IV

Thermodynamic constants for the ring inversion in CdI_2 (Et_4tds) and HgI_2 (Et_4tds) in $CDCl_3$*.

Compound	ΔE_{act} (kcal. mole^{-1})	$^{10}\log k_o$ (k_o in S^{-1})	$\Delta G^{\neq}_{273}$ (kcal. mole^{-1})	$\Delta H^{\neq}_{273}$ (kcal. mole^{-1})	$\Delta S^{\neq}_{273}$ (e.u.)
CdI_2 (Et_4tds)	13.0	14	11.5	12.5	4
HgI_2 (Et_4tds)	14.5	17	9.5	14.0	16

* The inaccuracy in ΔE_{act}, $\Delta G^{\neq}$ and $\Delta H^{\neq}$ is approximately 0.5 unit; for $^{10}\log k_o$ and $\Delta S^{\neq}$ approximately 1 unit.

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[5] *J. O. Sutherland*, Annual Reports on NMR spectroscopy, Vol. 4: Academic Press, London, 1971, p. 158.

[6] *H. C. Brinkhoff*, Ph. D. thesis, University of Nijmegen, The Netherlands, 1970.